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(54) **SELF-REFERENCING CAVITY ENHANCED SPECTROSCOPY (SRCES) SYSTEMS AND METHODS**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,412,676	A *	5/1995	Schnier	.....	H01S 3/1303 372/18
6,452,680	B1 *	9/2002	Paldus	.....	G01J 3/42 250/343
6,795,190	B1	9/2004	Paul et al.		
6,859,284	B2	2/2005	Rella et al.		
6,982,999	B1	1/2006	Richman et al.		
7,035,298	B2	4/2006	Vodopyanov et al.		
7,106,763	B2	9/2006	Tan et al.		
7,154,595	B2	12/2006	Paldus et al.		
7,173,754	B2	2/2007	Vodopyanov et al.		
7,259,856	B2	8/2007	Kachanov et al.		
7,265,842	B2	9/2007	Paldus et al.		
7,420,686	B2	9/2008	Tan		
7,535,573	B2	5/2009	Kachanov et al.		
7,646,485	B2	1/2010	Tan		
7,813,886	B2	10/2010	Tan		
7,902,534	B2 *	3/2011	Cole	.....	G01J 1/44 250/573
8,264,688	B1	9/2012	Tan		

(Continued)

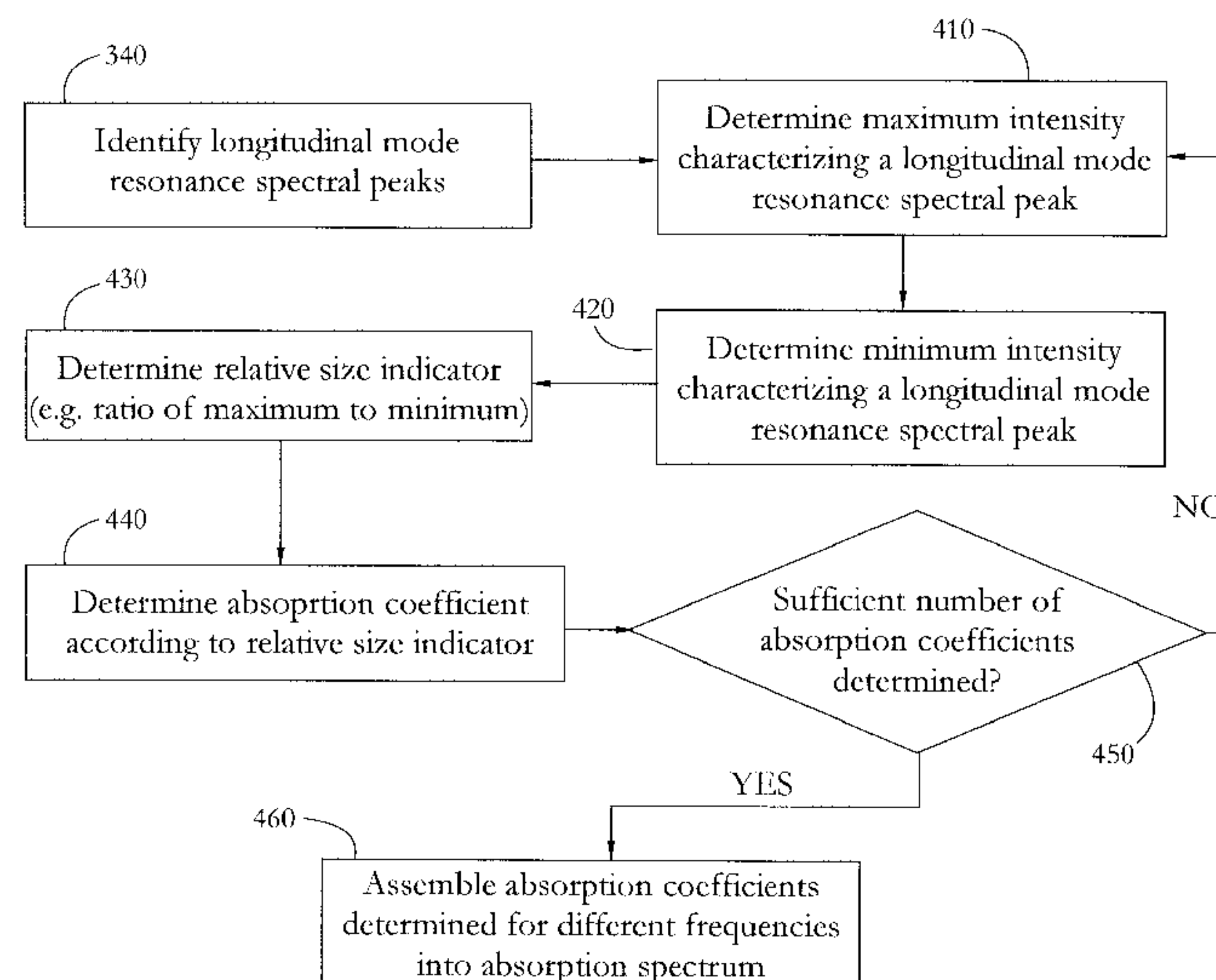
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(57) **ABSTRACT**

Described self-referencing cavity enhanced spectroscopy (SRCES) systems and methods are tailored to acquiring spectra in a middle regime, in which signals are lower than optimal for conventional absorption spectroscopy, and absorption is higher than optimal for cavity ring-down spectroscopy (CRDS). Longitudinal mode resonance spectral peaks are analyzed individually to extract intensity ratios (e.g. maximum to minimum) and/or curve-fitting parameters, obviating the need to measure or precisely control the input light intensity.

**39 Claims, 9 Drawing Sheets**



(56)                      **References Cited**

U.S. PATENT DOCUMENTS

8,537,362	B2	9/2013	He et al.	
8,982,352	B1	3/2015	Hoffnagle et al.	
9,116,047	B2 *	8/2015	Koulikov .....	G01J 3/45
2005/0012931	A1	1/2005	Tan et al.	
2005/0168826	A1	8/2005	Koulikov et al.	
2006/0083284	A1	4/2006	Paldus et al.	
2006/0181710	A1 *	8/2006	Kachanov .....	G01N 21/39
				356/437
2011/0216311	A1 *	9/2011	Kachanov .....	G01N 21/1702
				356/213
2013/0100973	A1 *	4/2013	Bondu .....	H01S 3/1392
				372/28
2014/0125993	A1 *	5/2014	Kachanov .....	G01J 3/26
				356/519

\* cited by examiner

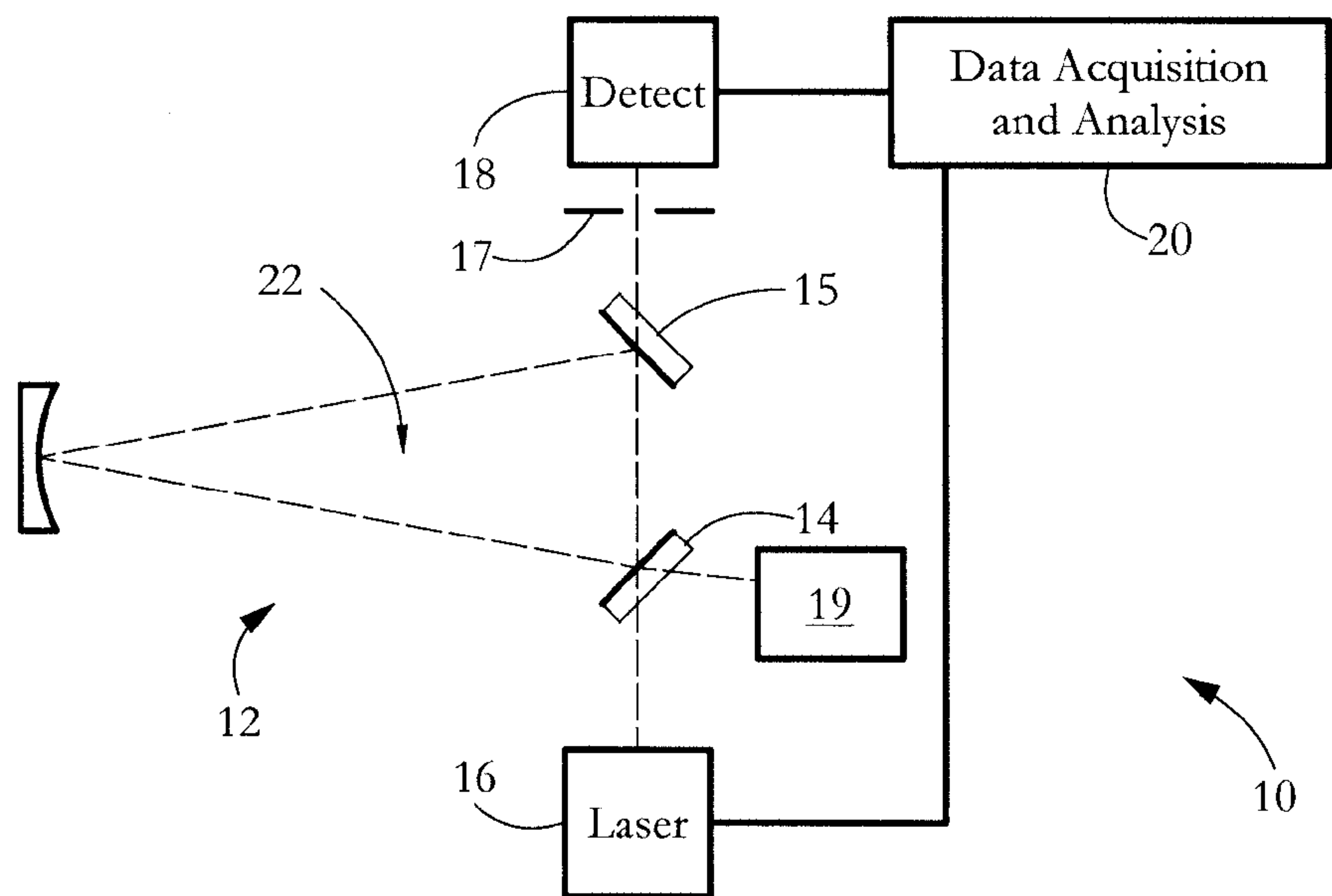


FIG. 1

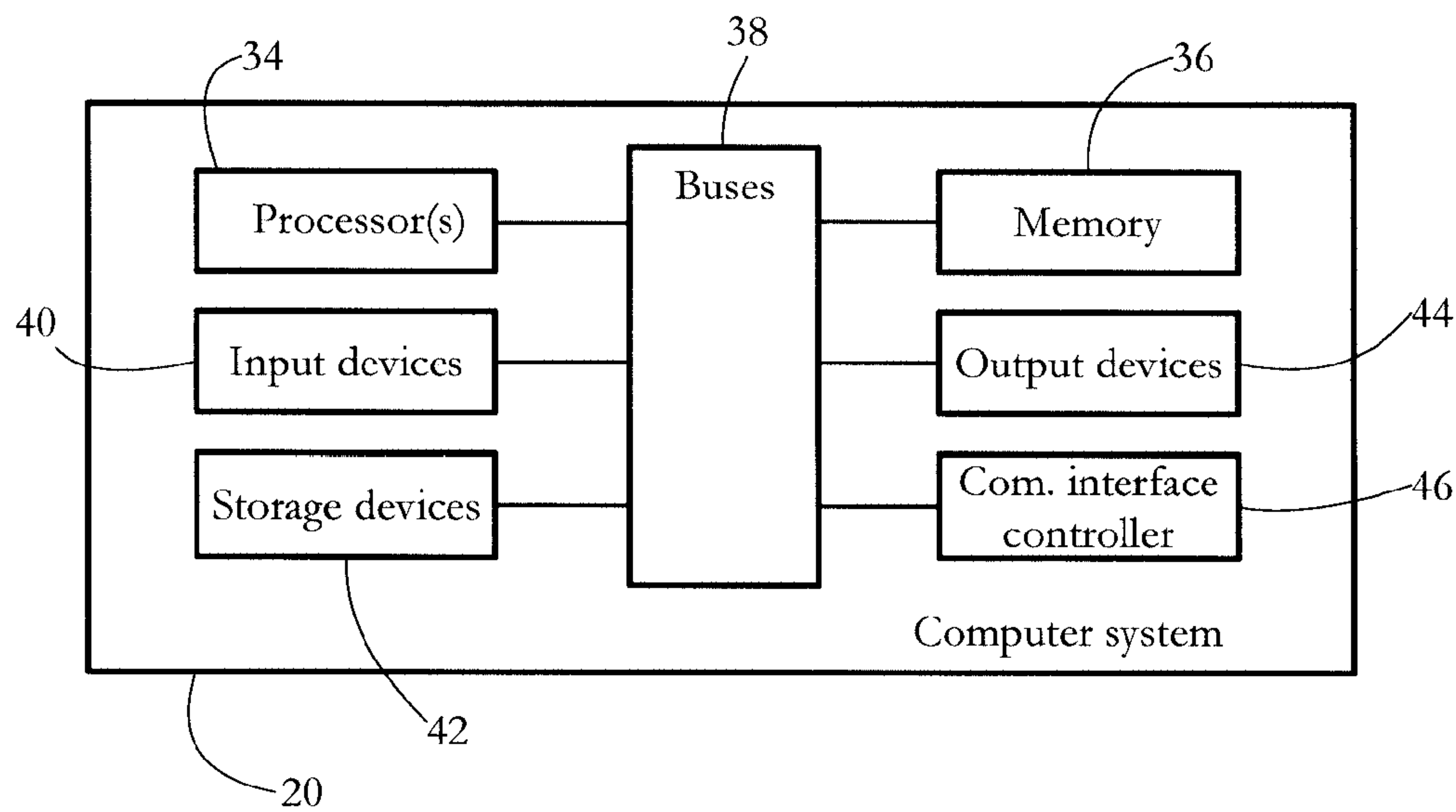


FIG. 2

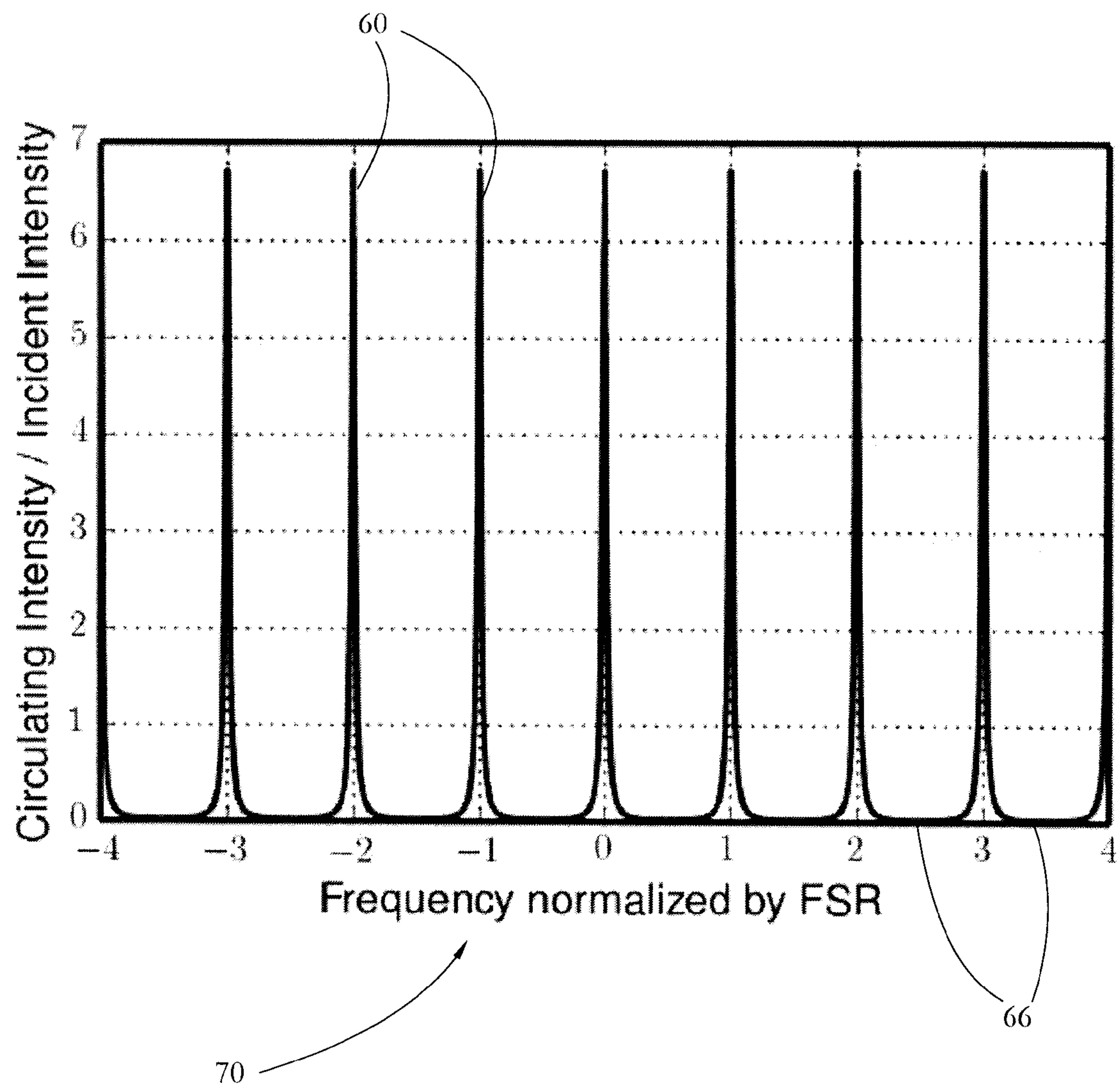


FIG. 3



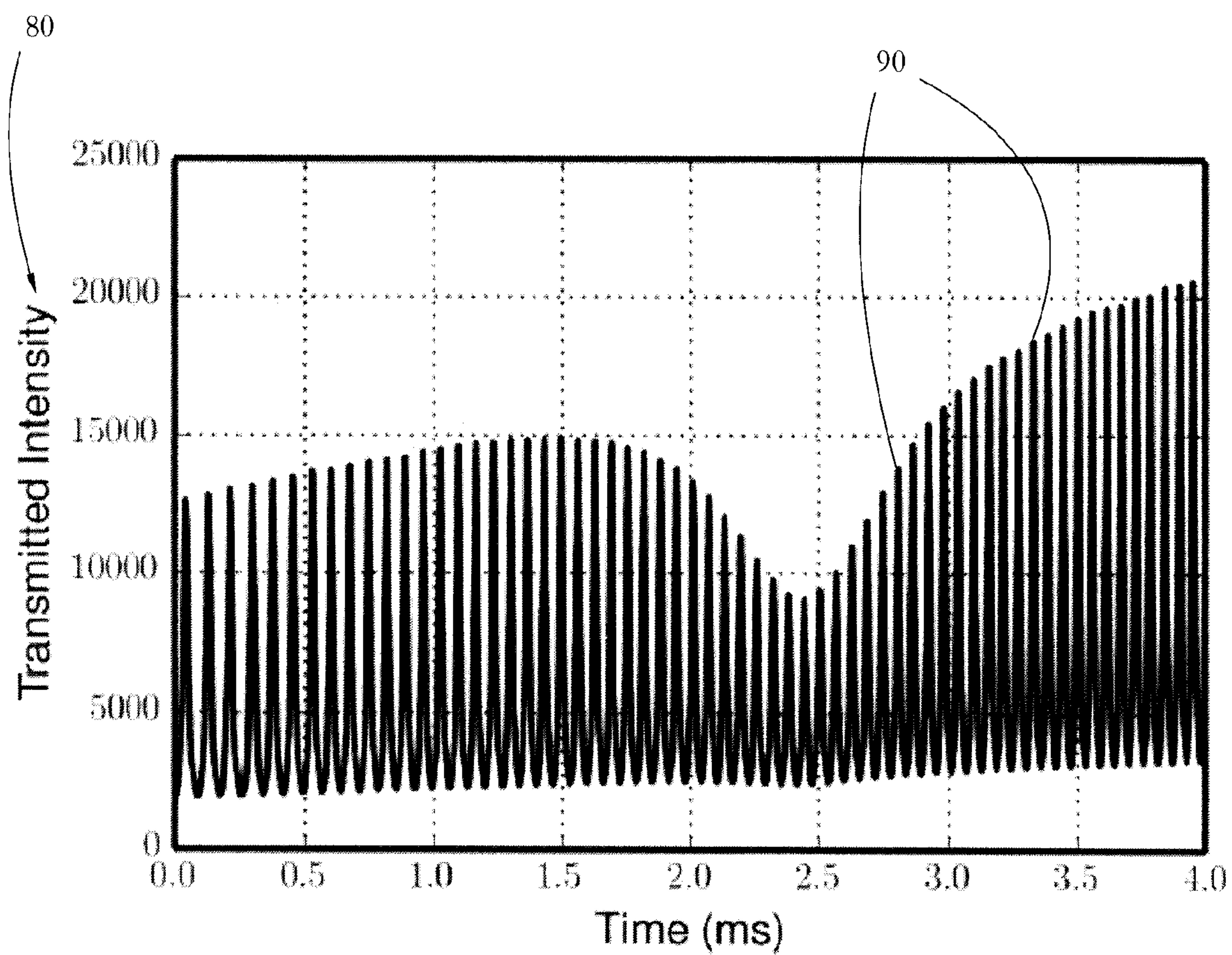


FIG. 4

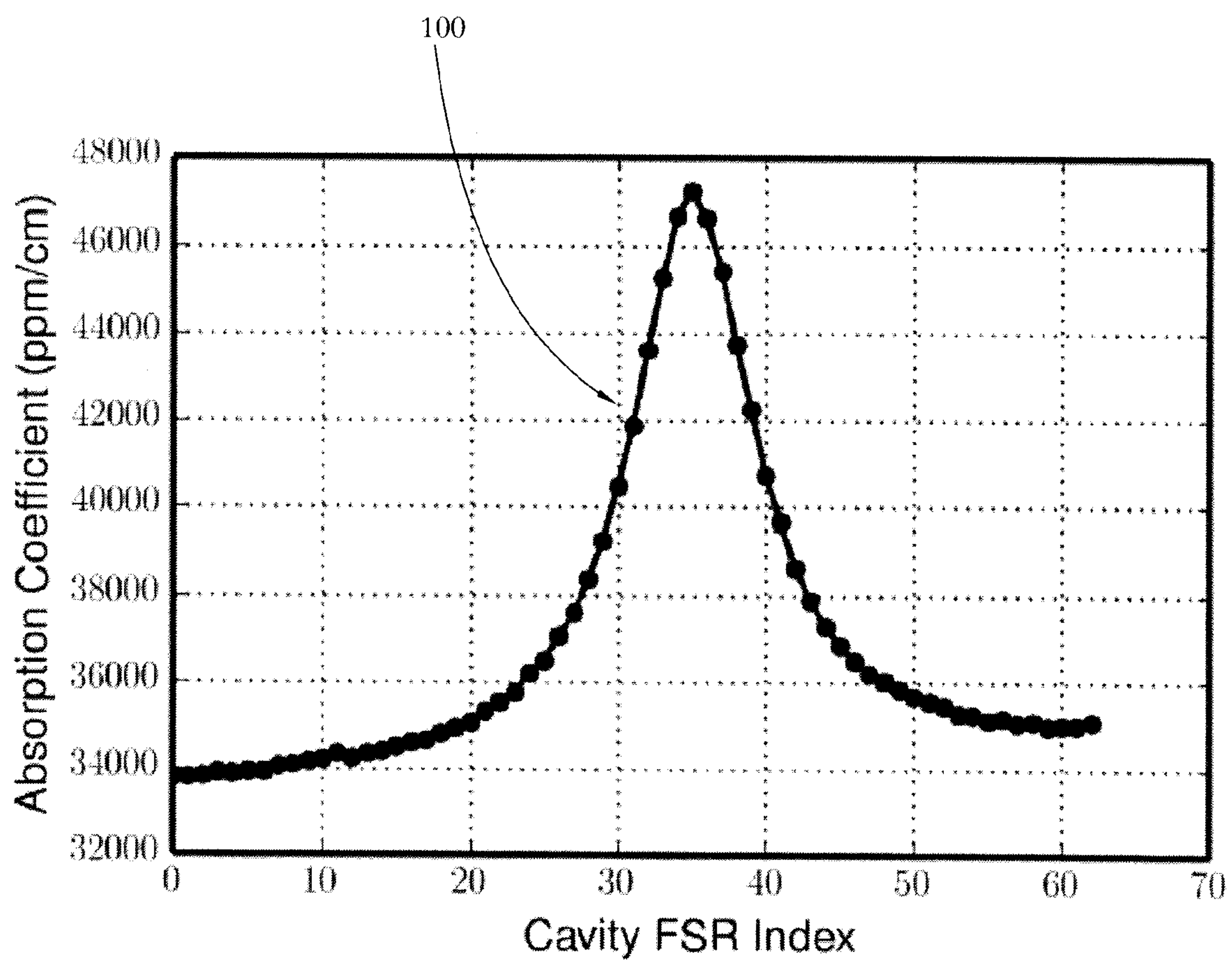


FIG. 5

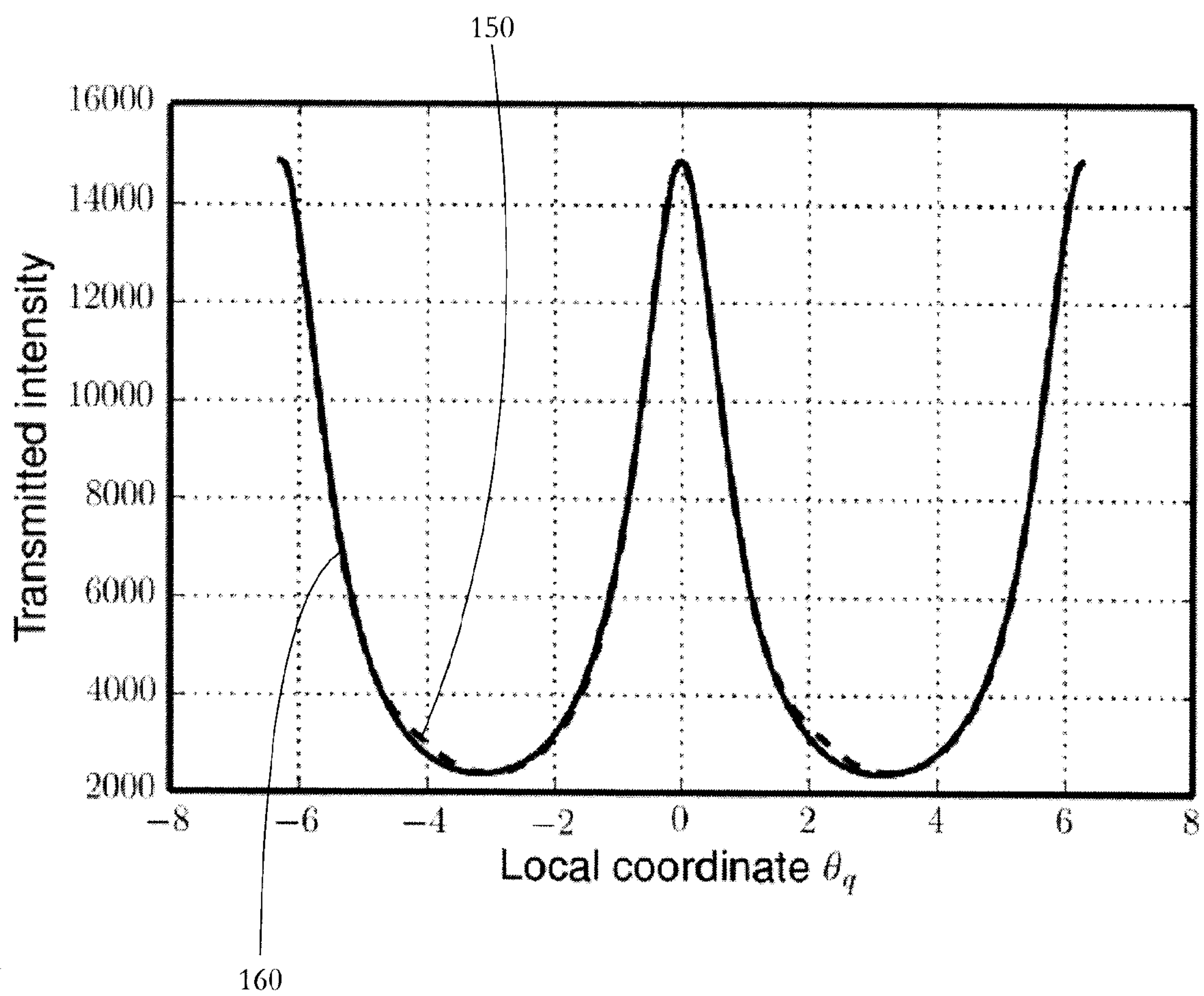


FIG. 6

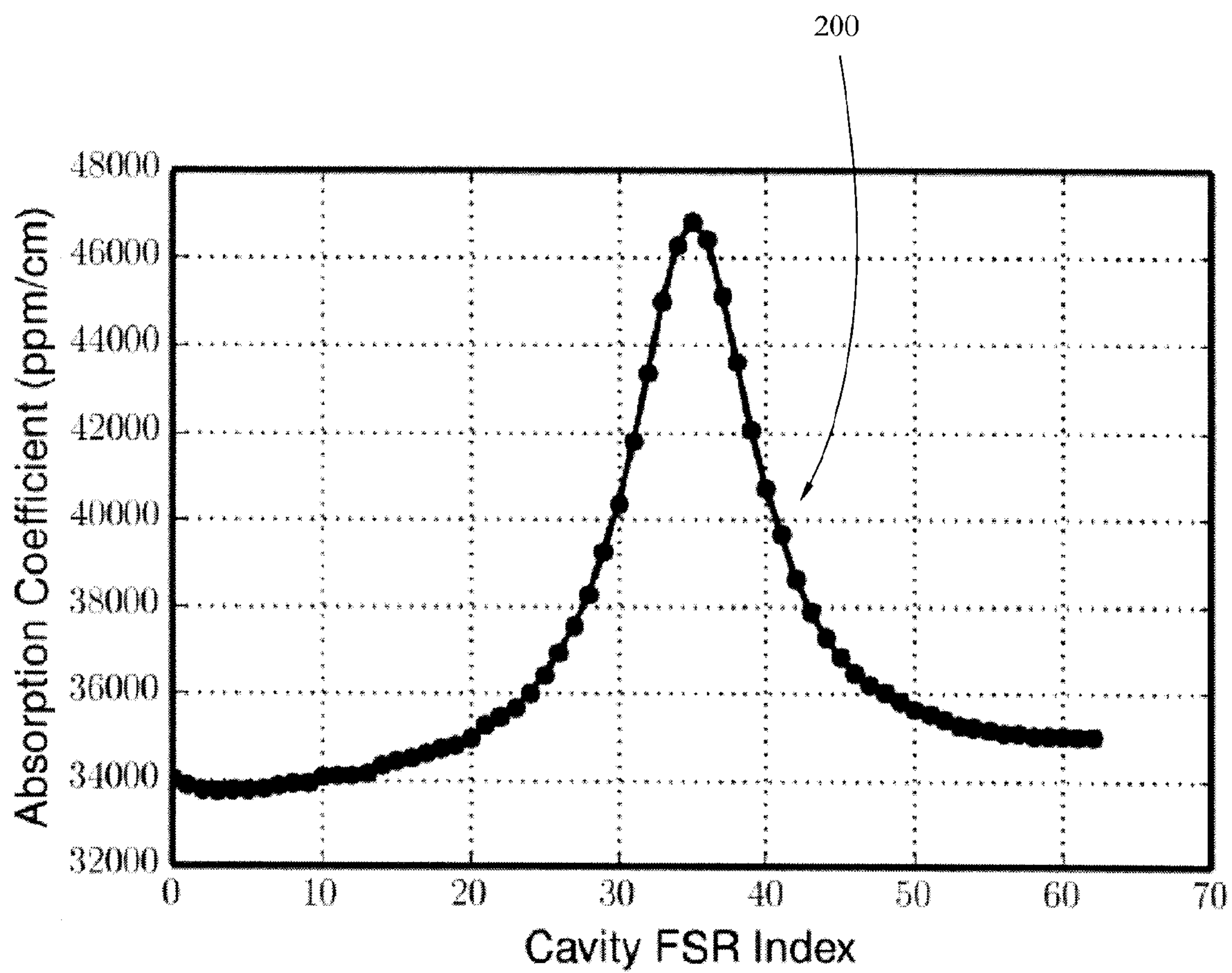


FIG. 7



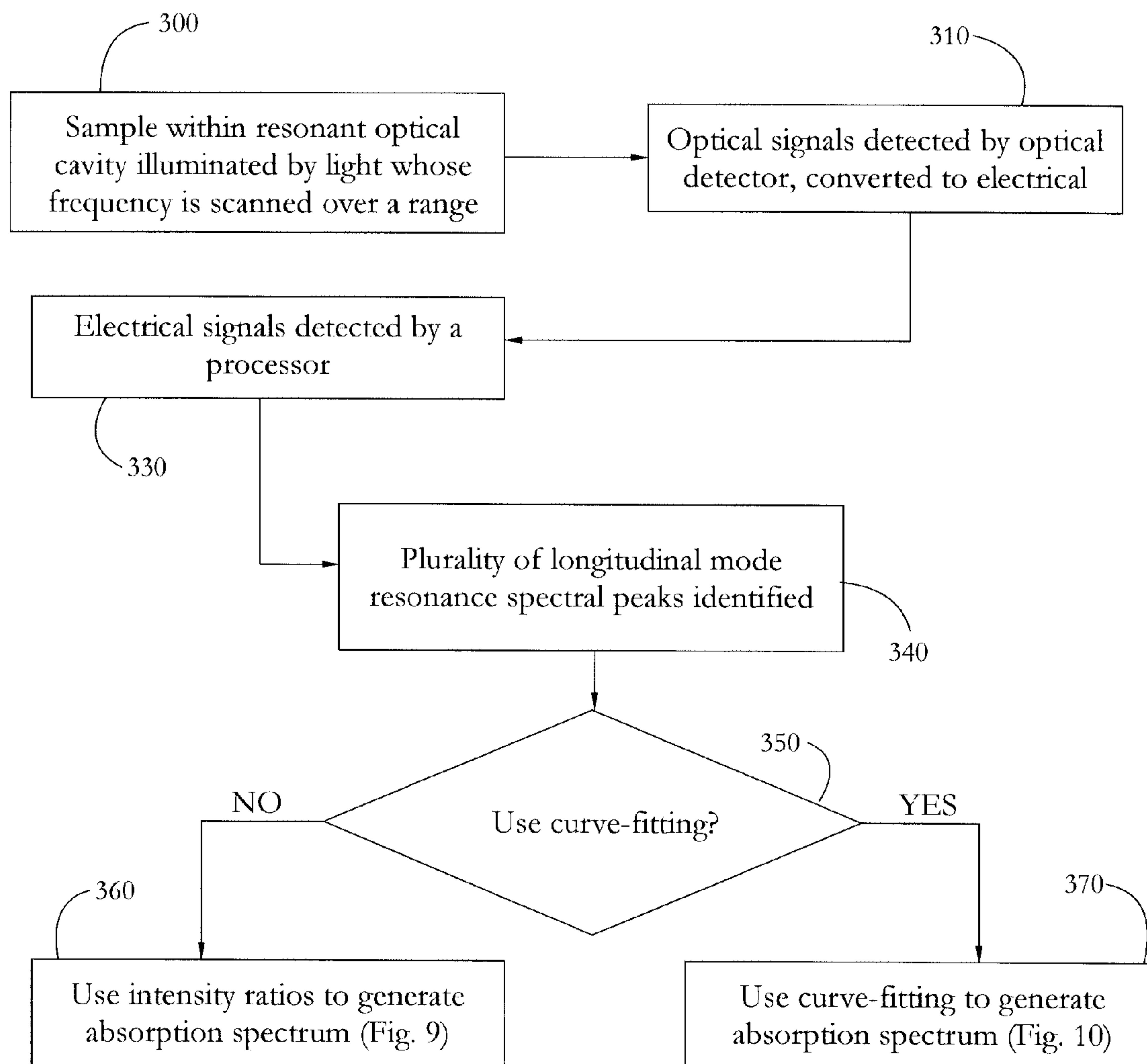


FIG. 8

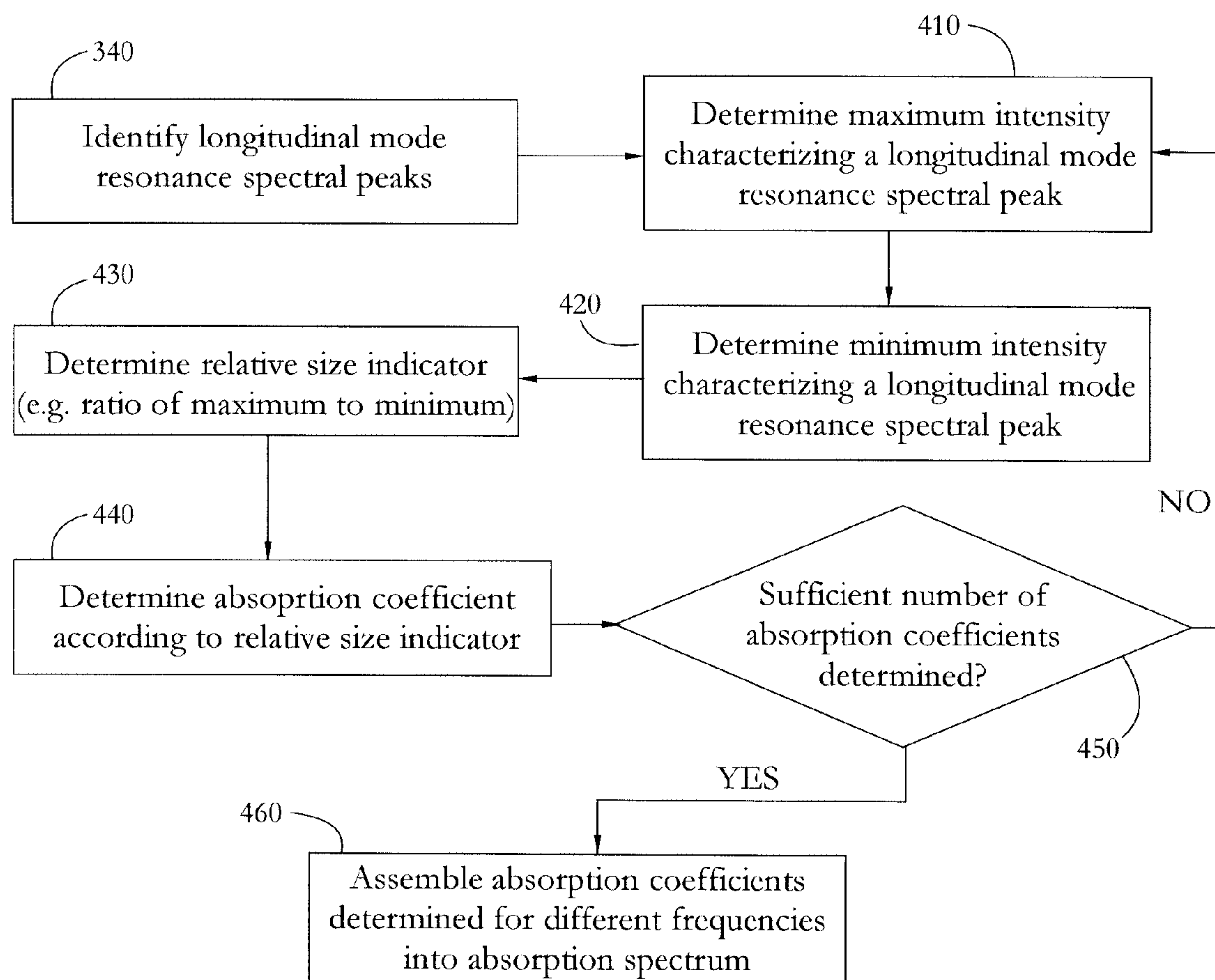


FIG. 9

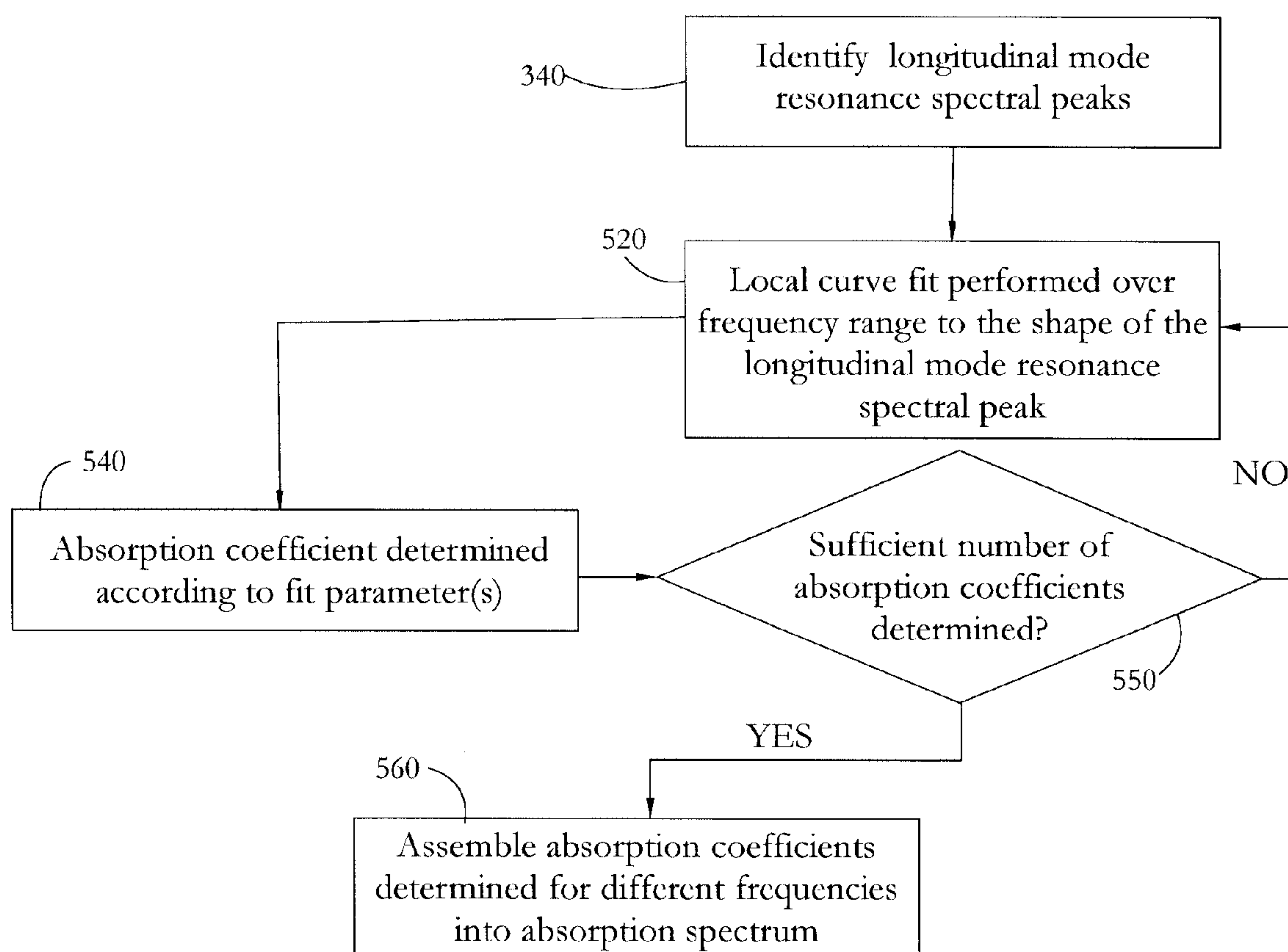


FIG. 10



# SELF-REFERENCING CAVITY ENHANCED SPECTROSCOPY (SRCES) SYSTEMS AND METHODS

## RELATED APPLICATION DATA

This application claims the benefit of the filing date of U.S. Provisional Patent Application No. 61/981,112, filed Apr. 17, 2014, which is herein incorporated by reference.

## BACKGROUND

The invention relates to systems and methods for performing spectroscopy.

A number of conventional spectroscopy techniques are used to analyze samples through the study of an interaction between the sample and light. These conventional techniques include direct absorption spectroscopy and cavity ring-down spectroscopy (CRDS). Direct absorption spectroscopy involves directly measuring an intensity transmission through an optical cavity with a sample, and comparing the results to a measured intensity transmission through an empty optical cavity. The absorption of light by the sample changes as a function of frequency, which enables the generation of an absorption spectrum of the sample. Direct absorption spectroscopy is effective when measuring relatively large amount of sample and/or a sample that interacts strongly with light. Direct absorption spectroscopy becomes less effective when analyzing a small amount of sample and/or a sample that interacts weakly with light. For such measurements, CRDS is generally more effective. CRDS measures ringdown times, i.e. amounts of time it takes for light that excites a resonant optical chamber and interacts with a sample to decay to a fraction of its initial intensity, for example  $1/e$ . An absorption spectrum can be generated from measured ring-down times.

## SUMMARY

According to one aspect, a spectroscopy apparatus comprises: a resonant optical cavity configured to hold a sample; an optical detector configured to detect optical signals emitted from the optical cavity and generate electrical signals from the optical signals, the optical signals defining a plurality of intensity values characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and a processor electrically connected to the optical detector and configured to determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak.

According to another aspect, a non-transitory computer-readable medium stores instructions which, when executed by a hardware processor, cause the processor to: receive electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak.

According to another aspect, a computer system comprises a hardware processor and associated memory configured to: receive electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak.

According to another aspect, a method comprises: receiving electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and determining, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak.

## BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing aspects and advantages of the present invention will become better understood upon reading the following detailed description and upon reference to the drawings where:

FIG. 1 illustrates an exemplary spectroscopy system according to some embodiments of the present invention.

FIG. 2 illustrates a plurality of hardware components of the system of FIG. 1 according to some embodiments of the present invention.

FIG. 3 depicts an idealized frequency response of a resonant optical cavity when excited by a laser according to some embodiments of the present invention.

FIG. 4 shows a result of measuring the light transmitted through a low-finesse,  $F \approx 3.8$ , resonant optical cavity with a round-trip length  $p = 48.5$  cm containing room air at atmospheric pressure according to some embodiments of the present invention.

FIG. 5 shows an absorption spectrum derived from maximum-minimum intensity ratios according to some embodiments of the present invention.

FIG. 6 depicts a curve-fitting process performed on a longitudinal mode resonance spectral peak according to some embodiments of the present invention.

FIG. 7 shows an absorption spectrum derived from fitting mode resonances according to some embodiments of the present invention.

FIG. 8 depicts an exemplary sequence of steps performed by a spectroscopy system according to some embodiments of the present invention.

FIG. 9 shows an exemplary series of steps executed by a processor to generate a sample absorption spectrum using intensity ratio analysis according to some embodiments of the present invention.

FIG. 10 shows an exemplary series of steps executed by a processor to generate a sample absorption spectrum using curve-fitting according to some embodiments of the present invention.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Systems and methods described herein may include or employ one or more spectrometers including control/acqui-



sition computer systems as described below. In the following description, it is understood that all recited connections between structures can be direct operative connections or indirect operative connections through intermediary structures. A set of elements includes one or more elements. Any recitation of an element is understood to refer to at least one element. A plurality of elements includes at least two elements. Unless otherwise required, any described method steps need not be necessarily performed in a particular illustrated order. A first element (e.g. data) derived from a second element encompasses a first element equal to the second element, as well as a first element generated by processing the second element and optionally other data. Making a determination or decision according to a parameter encompasses making the determination or decision according to the parameter and optionally according to other data. Unless otherwise specified, an indicator of some quantity/data may be the quantity/data itself, or an indicator different from the quantity/data itself. Computer readable media encompass storage (non-transitory) media such as magnetic, optic, and semiconductor media (e.g. hard drives, optical disks, flash memory, DRAM), as well as communications links such as conductive cables and fiber optic links. According to some embodiments, the present invention provides, inter alia, optical systems such as spectrometers including computer systems programmed to perform methods described herein, as well as computer-readable media encoding instructions to perform methods described herein.

FIG. 1 depicts an exemplary optical system 10 according to some embodiments of the present invention. Optical system 10 may be a spectrometer. Optical system 10 includes a resonant optical cavity 12 comprising two or more mirrors including an input mirror 14 and an output mirror 15, a laser light source 16 in optical communication with cavity 12, an optical detector 18 optically connected to cavity 12, and a data acquisition and analysis computer system 20 electrically connected to source 16 and detector 18. Resonant optical cavity 12 is configured to hold a sample 22. Source 16 is configured to send monochromatic light into cavity 12. Source 16 may include or be optically coupled to a dedicated photodetector or other device capable of measuring the optical power produced by source 16, as well as a dedicated high-precision wavelength monitor capable of measuring the exact wavelength of light emitted by source 16. Detector 18 is configured to detect optical signals emitted from cavity 12. Data acquisition and analysis computer system 20 is configured to perform a number of control and data acquisition and analysis steps described below. In particular, computer system 20 may be used to control a frequency of light emitted by source 16, and analytical methods performed by computer system 20 as described below are used to characterize samples of interest placed within cavity 12.

In some embodiments, optical system 10 may be designed so as to minimize the impact of higher-order transverse modes on detected signals, and in particular on the intensity detected for frequencies along longitudinal mode inter-peak minima, described below. Higher-order transverse modes may have slightly different resonant frequencies than the TEM<sub>00</sub> Gaussian mode, and thus may cause undesired effects on detected intensities, particularly for frequencies along minima between different longitudinal mode peaks. In some embodiments cavity 12 may be confocal cavity, i.e. a cavity characterized by a mirror radius of curvature R equal to a cavity length L. Confocal cavities may be characterized by degenerate higher-order transverse modes and may exhibit particularly clean (smoothly varying) intensity

maxima and minima, and in particular may exhibit less variation in intensity along inter-peak intensity minima. Additionally, in some embodiments an optical spatial filter 17 is positioned in an optical path between cavity 12 and detector 18. Spatial filter 17 may be a pinhole or other spatial obstruction configured to filter out higher-order cavity transverse modes. Also, in some embodiments focusing and beam steering optics positioned in the optical path between source 16 and cavity 12 may be used to match the spatial mode of the input laser beam to the fundamental TEM<sub>00</sub> Gaussian mode of cavity 12, to minimize the potential effects of transverse mode resonances.

In some embodiments, a second optical detector 19 may be used to detect input light incident from source 16 and reflected by input mirror 14. Because the light reflected by input mirror 14 is due to the summed electric fields of the reflected input beam and transmitted intracavity power, information related to the wavelength spectrum of the input beam, including the linewidth and the tuning rate, is embedded in the reflected signal. Signals from second optical detector 19 may be used to decouple the effect of the linewidth of source 16 from transmitted signals detected by detector 18, effectively separating detected intensity variations caused by cavity 12 from those caused by fluctuations in the intensity of light emitted by source 16. Additionally, in some embodiments, signals from a dedicated photodetector and dedicated high-precision wavelength monitor forming part of (or coupled to) light source 16 may also be used to improve the quality of the spectral data collected by the apparatus.

In some embodiments, a calibration procedure performed on a cavity without a sample, and/or at wavelength(s) at which the sample does not have a significant absorption, may be used to determine a relationship between the signals received from second detector 19 and adjustments to be performed on the collected spectral data for different measurement conditions. In some embodiments, the calibration procedure includes performing measurements on an empty cavity, for different scanning speeds and different input laser linewidths, to determine how the reflected signal detected by second detector 19 and the output signal detected by detector 18 depend on scanning speed, input laser linewidth, and/or other calibration parameter(s) of interest. The results of the calibration procedure may be used in conjunction with data obtained from second detector 19 and/or the optical power and wavelength monitors of source 16 to correct the spectral data collected using detector 18, in order to reduce the effects of extraneous factors on the spectral data of interest.

In some embodiments, computer system 20 comprises a plurality of hardware components, schematically illustrated in FIG. 2. In some embodiments, computer system 20 comprises one or more processors 34, a memory unit 36, a set of input devices 40, a set of output devices 44, a set of storage devices 42, and a communication interface controller 46, all connected by a set of buses 38. In some embodiments, processor 34 comprises a physical device (e.g. multi-core integrated circuit) configured to execute computational operations with a set of signals and/or data. In some embodiments, such computational operations are delivered to processor 34 in the form of a sequence of processor instructions (e.g. machine code or other type of software). Memory unit 36 may comprise random-access memory (RAM) storing instructions and operands accessed and/or generated by processor 34. Input devices 40 may include touch-sensitive interfaces, computer keyboards and mice, among others, allowing a user to introduce data and/or instructions into system 18. Output devices 44 may include display devices



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such as monitors. In some embodiments, input devices **40** and output devices **44** may share a common piece of hardware, as in the case of touch-screen devices. Storage devices **42** include computer-readable media enabling the storage, reading, and writing of software instructions and/or data. Exemplary storage devices **42** include magnetic and optical disks and flash memory devices, as well as removable media such as CD and/or DVD disks and drives. Communication interface controller **46** enables system **18** to connect to a computer network and/or to other machines/computer systems. Typical communication interface controllers **46** include network adapters. Buses **38** collectively represent the plurality of system, peripheral, and chipset buses, and/or all other circuitry enabling the inter-communication of devices **34-46** of computer system **18**.

In some embodiments, the frequency of light emitted by laser light source **16** is scanned, linearly or otherwise, over a range of values large enough to encompass multiple longitudinal mode resonance peaks. Scanning the frequency of monochromatic light emitted by source **16** may be achieved under the control of computer system **20** by ramping a source current of source **16** or other known methods.

Cavity **12** houses a sample **22** of interest, which may be in gaseous, solid or liquid form. If the composition of sample **22** within cavity **12** is kept fixed and the current waveform used is periodic in time, the intracavity intensity of light is not necessarily periodic with time even after all transients have died away, because a major component of a laser linewidth of source **16** is due to stochastic processes which do not repeat in time. Although the results for individual periods differ, an average over many periods may be computed and this average converges to a deterministic mean value, which can be compared with theoretical predictions. The rate of convergence depends on the relative linewidths of cavity **12** and source **16**. When the linewidth of cavity **12** is large compared to the linewidth of source **16**, a convergence to the mean is fast, so this is the regime in which the comparison of the average over many periods to theoretical predictions is expected to be most successful.

FIG. **3** depicts an idealized frequency response of cavity **12** when excited by source **16** according to some embodiments of the present invention. The data of FIG. **3** are determined according to equation (1):

$$\frac{I_{circ}}{I_{inc}} = \frac{|t|^2}{|1 - r \exp(-\alpha p - j2\pi\nu p/c)|^2} \quad (1)$$

In equation (1),  $t$  is an amplitude transmission coefficient of input mirror **14** and  $r$  is a product of multiple amplitude reflection coefficients of all mirrors comprising cavity **12**. In equation (1),  $\alpha$  represents a sample absorption coefficient,  $p$  is a round-trip length of cavity **12**, and  $\nu$  is a frequency of incident light generated by source **16**. The variables  $t$ ,  $r$ , and  $\alpha$  may be taken to be frequency-independent in the discussion below.

As seen in FIG. **3**, maxima **60** of a circulating intensity occur close to the frequencies at which  $r \exp(-j2\pi\nu p/c)$  is real and positive, and minima **66** occur close to the frequencies at which  $r \exp(-j2\pi\nu p/c)$  is real and negative. Successive maxima **60** (or minima **66**) are spaced by the cavity free spectral range  $\nu_{FSR}=c/p$ . Each maximum is the center of a peak whose full width at half maximum is given by equation (2) below:

## 6

$$(\Delta\nu)_{FWHM} = \frac{2c}{\pi p} \sin^{-1} \left( \frac{1-r'}{2\sqrt{r'}} \right) = \frac{(\Delta\nu)_{FSR}}{\mathcal{F}} \quad (2)$$

In equation (2),  $r'=r \exp(-\alpha p)$  represents an amplitude change over a round-trip due to both mirror losses and a material absorption of the sample, and

$$\mathcal{F} = \left[ \frac{2}{\pi} \sin^{-1} \left( \frac{1-r'}{2\sqrt{r'}} \right) \right]^{-1} \quad (3)$$

represents a finesse, defined as a ratio of a free spectral range to a full width at half maximum. If cavity **12** is used in a ring-down spectrometer, the equivalent ring-down time is  $\tau=[2\pi(\Delta\nu)_{FWHM}]^{-1}$ . We may use a circulating intensity in equation (1) even though in practice we may measure a transmitted intensity in practice. The circulating intensity and the transmitted intensity are generally related by a proportionality constant.

Equation (1) represents a steady-state result, computed on the assumption that the frequency of the incident light is constant. When the frequency of the light is swept linearly through resonances at a rate of  $R \text{ Hz s}^{-1}$ , equation (1) may still be applied quasi-statically using the instantaneous frequency for  $\nu$ , provided the dimensionless quantity  $\pi(\Delta\nu)_{FWHM}^2/R \gg 1$ . When the above condition is met, the optical energy in the cavity can achieve full resonance before the frequency of the laser shifts appreciably, or in other words, the chirp is slow enough that the change in instantaneous frequency of the light over the decay time of the cavity is small compared to the cavity linewidth.

According to some embodiments of the present invention, sample absorption coefficients are determined by analyzing individual cavity longitudinal mode spectral peaks, so as to obviate the need to measure or precisely control the input light intensity. Such methods, referred-to below as self-referencing cavity enhanced spectroscopy (SRCES), include methods employing intensity ratio analysis and curve-fitting analysis as described below.

#### Intensity Ratio Analysis

According to some embodiments of the present invention, one type of SRCES uses a ratio of a maximum intensity characterizing a longitudinal mode resonance spectral peak to a minimum intensity characterizing the longitudinal mode resonance spectral peak. Such a method partitions a measured transmitted intensity spectrum as shown in FIG. **4** into local pieces, each piece encompassing a longitudinal mode resonance spectral peak. Subsequently, locating the maximum intensity characterizing the longitudinal mode resonance spectral peak and the minimum intensity characterizing the longitudinal mode resonance spectral peak may be done by performing localized curve fitting near the maximum or minimum of the peak, by selecting one experimentally measured maximum or minimum point of the peak, or by another method that converts the measured data points into a value representing a peak maximum or minimum. The maximum intensity characterizing a longitudinal mode resonance spectral peak can be represented by equation (4):

$$\frac{(I_{circ})_{max}}{I_{inc}} = \frac{|t|^2}{|1 - r \exp(-\alpha p)|^2} \quad (4)$$



A corresponding minimum intensity characterizing a longitudinal mode resonance spectral peak can be represented by equation (5):

$$\frac{(I_{circ})_{min}}{I_{inc}} = \frac{|t|^2}{|1 + r \exp(-\alpha p)|^2}. \quad (5)$$

Although the frequencies at which a maximum and its adjacent minimum occur may be separated by the cavity free spectral range, it is often the case that the quantities  $I_{inc}$ ,  $t$ ,  $r$  and  $\alpha$  do not change an appreciable amount between adjacent extrema in some embodiments of the present invention. As a result, a ratio of the maximum intensity characterizing a longitudinal mode resonance spectral peak to the minimum intensity characterizing a longitudinal mode spectral peak may be determined using equation (6):

$$\rho = \frac{(I_{circ})_{max}}{(I_{circ})_{min}} = \frac{|1 + r \exp(-\alpha p)|^2}{|1 - r \exp(-\alpha p)|^2} = \frac{|1 + r'|^2}{|1 - r'|^2} \quad (6)$$

The ratio may also be determined using an average of adjacent maximum intensities as the maximum intensity characterizing the peak and/or an average of adjacent minimum intensities as the minimum intensity characterizing the peak, according to some embodiments of the present invention. Furthermore, a value of an amplitude change over a round-trip due to both mirror losses and a material absorption of the sample may be determined from the ratio  $\rho$  as shown in equation (7):

$$r' = \frac{\sqrt{\rho} - 1}{\sqrt{\rho} + 1} \quad (7)$$

According to some embodiments of the present invention, an absorption coefficient due to the reflective surfaces and the material within the cavity may be computed using equation (8) shown below.

$$2\alpha' = -\frac{2}{p} \log r' = -\frac{2}{p} \log \frac{\sqrt{\rho} - 1}{\sqrt{\rho} + 1} \quad (8)$$

An intensity ratio,  $\rho$ , and a round trip path length,  $p$ , may be extracted from experimental data as described above. FIG. 4 depicts a result of measuring the transmitted intensity **80** through a low-finesse,  $F \approx 3.8$ , cavity with a round-trip length  $p = 48.5$  cm containing room air at atmospheric pressure according to some embodiments of the present invention. The laser light source was a distributed feedback (DFB) laser with a nominal wavelength of  $1.391 \mu\text{m}$ , near which water vapor exhibits a number of strong absorption features. The temperature of the laser light source was stabilized while the laser current was modulated by a triangular wave that swept the frequency of the emitted light over  $1 \text{ cm}^{-1}$  in 3.5 ms. The output intensity was measured using an optical detector sampled at a rate of 2.5 MHz, and an average over 100 scan cycles was computed. Positions and values of local extrema **90** were located and determined by fitting a parabola through a collection of nine samples closest to each extremum. In some embodiments, positions and values of

local extrema **90** may also be located by selecting the experimentally measured maximum or minimum point of the peak.

Total loss due to cavity reflective surfaces and sample inside the cavity may be computed using equation (8) from a collection of intensity ratios defined by extrema **90**, according to some embodiments of the present invention. FIG. 5 depicts a spectrum **100** of a total absorption coefficient generated according to equation (2). The horizontal (frequency) axis is labeled according to the longitudinal mode index. If the longitudinal mode index is known to be equally spaced by a cavity free spectral range (FSR), the frequency values corresponding to the longitudinal mode index may be known with precision.

#### Curve Fitting Analysis

According to some embodiments of the present invention, a sample absorption coefficient may be determined by fitting a curve to a shape of a longitudinal mode resonance spectral peak over a determined frequency range. In the experimental example presented above, in which an absorption coefficient was determined by intensity ratios, the cavity was so lossy, with an effective ring-down time of 1 ns, that the transmitted intensity at each local minimum was still large enough to be accurately measured. Due to the relatively large transmitted intensity, it was possible to measure the ratio of maximum to minimum transmitted intensity with reasonable precision and use ratios to derive a meaningful absorption coefficient. In the case of a less lossy cavity, for example one with a ring-down time of 30 ns and round trip path length of  $p = 48.5$  cm, the ratio of maximum to minimum intensity may be relatively large (e.g. 1700). Measuring such a large intensity ratio precisely may be challenging, requiring the use of high dynamic range data acquisition electronics or perhaps several processing channels with different gains to capture both the maxima and minima effectively. An additional problem can arise from the parasitic excitation of transverse modes in the cavity, which can raise the minimum intensities to such an extent that intensity ratios become inaccurate. If intensity ratios are inaccurate, it may be preferable to make more careful use of the detailed shape of a mode resonance as described below.

Consider a range of frequencies extending over two cavity free spectral ranges and centered about a longitudinal mode resonance  $\nu_q$ , where  $q$  is an integer index. It may be convenient to rewrite equation (1) in terms of a variable  $\theta_q = 2\pi(\nu - \nu_q)p/c$  which is zero at  $\nu_q$  and varies from  $-2\pi$  to  $+2\pi$  over the range of interest. This substitution may be written as shown below.

$$\frac{I_{circ}}{I_{inc}} = \frac{|t|^2}{|1 - r' \exp(-j\theta_q)|^2} = \frac{|t|^2}{1 - 2r' \cos \theta_q + r'^2} \quad (9)$$

Equation (9) can then be solved to show a transmitted intensity as shown below in equation (10):

$$I_{trans} = \frac{A}{1 - 2r' \cos \theta_q + r'^2}. \quad (10)$$

In equation (10),  $A$  is a factor which depends on the intensity of incident light, the proportionality between transmitted and circulating intensities, and a value of  $|t|^2$ . If  $A$  and



$r'$  are approximately constant over a range  $\theta_q \in (-2\pi, 2\pi)$ , we may use curve fitting analysis to determine  $r'$  and  $A$  from the measurements of  $I_{trans}$ .

Starting from the average measured transmitted intensity shown in FIG. 4 we may consider local extrema in turn and identify the local extrema as corresponding to transverse mode resonances at frequency  $\nu_g$  for successive values of  $q$ , according to some embodiments of the present invention. The interval from  $\nu_{q-1}$  to  $\nu_{q+1}$  may be mapped linearly to the interval  $(-2\pi, 2\pi)$  and the local extrema **90** may be used as data for a least-squares fitting problem using the model of equation (10). In effect, it may be assumed that over a small frequency range, the relationship between time and laser frequency is approximately linear. Since the relationship between time and laser frequency may not be precisely linear, it may be useful to introduce an additional parameter into the fit in order to allow the value of  $\theta_q$  to be offset so as to better fit the data.

FIG. 6 depicts a result of a least-squares fit performed on the optical cavity mode spectrum around a particular longitudinal mode resonance spectral peak. Dashed curve **150** depicts the unmodified data, while solid curve **160** depicts the best fitting model. It may be seen from FIG. 6 that the fit is generally good, except for the presence of an additional transverse mode which is seen in a residual between dashed curve **150** and solid curve **160**. A sample absorption coefficient may be determined from the fit parameter(s) of solid curve **160**.

FIG. 7 depicts an absorption spectrum **200** derived from curve fitting longitudinal mode resonance spectral peaks as illustrated in FIG. 6. By successively performing a sequence of curve fits for each longitudinal mode resonance spectral peak and deriving an absorption coefficient from fit parameter  $r'$ , a graph similar to FIG. 7 may be derived according to some embodiments of the present invention. A method employing curve-fitting performed on longitudinal mode resonance spectral peaks may be preferred over a method employing maximum/minimum intensity ratios when resonances are sharp and the intensity minima have relatively low values. The exemplary curve-fitting method depicted in FIG. 7 fits the entire shape or at least a significant part (e.g. a majority) of the mode resonance peak, rather than merely a ratio of intensities of extrema as shown in FIG. 5.

FIG. 8 depicts an exemplary sequence of steps performed by a spectroscopy system according to some embodiments of the present invention. In a step **300**, a sample placed in a resonant optical cavity is illuminated by laser light whose frequency is scanned over a range of interest under the control of a computer system. In particular, the frequency range of interest encompasses a plurality of longitudinal mode resonance spectral peaks. An interaction of the sample with the light introduced by the source affects optical signals that are emitted from the cavity.

In a step **310**, optical signals emitted from the cavity are detected by optical detector **18**, which generates corresponding electrical signals in response. In a step **330**, a processor of the computer system receives the electrical signals via the electrical connection between the computer system and the optical detector. The signals may be processed according to calibration data, signals received from second optical detector **19**, and power and wavelength data received from light source **16** in order to reduce the effect of extraneous factors such as scanning speed or input laser linewidth on the absorption spectrum determination.

The processor then identifies a plurality of longitudinal mode resonance spectral peaks defined by the electrical signals in a step **340**. In a step **350**, the processor determines

whether to use curve-fitting and/or intensity ratio analysis to generate an absorption spectrum as described above. The choice of analysis method may be performed according to a measured ring-down time of the resonant optical cavity with or without the sample present. In some embodiments, if the measured ring-down time is less than (or less than or equal to) a predetermined threshold a sample absorption spectrum is determined according to intensity ratio analysis as illustrated by a step **360**. If the measured ring-down time is greater than (or greater than or equal to) the predetermined threshold, then a sample absorption spectrum is determined according to curve fitting analysis, as illustrated by a step **370**. In some embodiments, the predetermined threshold has a value between 10 ns and 100 ns, for example between 20 ns and 50 ns, more particularly between 25 ns and 40 ns, specifically about 30 ns. An intensity ratio analysis method illustrated by step **360** is explained in further detail with reference to FIG. 9. A curve fitting analysis method illustrated by step **370** is explained in further detail with reference to FIG. 10.

FIG. 9 depicts an exemplary series of steps executed by a processor to generate a sample absorption spectrum using intensity ratio analysis according to some embodiments of the present invention. In a step **410**, a maximum intensity characterizing a longitudinal mode resonance spectral peak is determined. The maximum intensity may be determined by fitting a curve over a plurality of samples near the maximum of the longitudinal mode resonance spectral peak, by selecting the experimentally measured maximum value along the longitudinal mode resonance spectral peak, and/or by selecting one or more other points indicative of the intensity maximum and determining a maximum intensity from the selected values. In a step **420**, the processor determines a minimum intensity characterizing the longitudinal mode resonance spectral peak. The minimum intensity may be determined by fitting a curve over a plurality of samples near a minimum of the longitudinal mode resonance spectral peak, by selecting an experimentally measured minimum value along the longitudinal mode resonance spectral peak, and/or by selecting one or more other points indicative of the intensity minimum and determining a minimum intensity from the selected values. In some embodiments, localized curve-fitting to determine local extrema may be performed using a parabolic function and a predetermined number (e.g. 5-15, for example about nine) of samples. In a step **430**, the processor determines an indicator of the relative size of the maximum and minimum peak values, for example a ratio of the maximum intensity to the minimum intensity. In a step **440**, a sample absorption coefficient for a given frequency is determined according to the relative size indicator, as described above.

In a step **450**, the processor determines whether or not a condition has been met in order to generate a sample absorption spectrum. If absorption coefficients have not yet been determined for an entire predetermined frequency range of interest, another longitudinal mode spectral peak at the next different frequency is analyzed. In this case, the processor begins again at step **410** resulting in the determination of another sample absorption coefficient at step **440** according to another intensity ratio analysis. Once absorption coefficient values spanning the frequency range of interest have been determined, the absorption coefficients are assembled into a spectrum for the frequency range of interest, as illustrated by a step **460**.

FIG. 10 depicts an exemplary series of steps executed by a processor to generate a sample absorption spectrum using curve fitting analysis according to some embodiments of the



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present invention. In a step 520, the processor performs a curve fit to a shape of an identified longitudinal mode resonance spectral peak. The peak extent used for curve-fitting may be defined by a frequency range extending over two cavity free spectral ranges and centered at the frequency of the peak maximum. Step 520 results in the determination of one or more curve fit parameters, as described above. In a step 540, a sample absorption coefficient is determined from the fit parameter(s).

In a step 550, the processor determines whether or not a condition has been met in order to generate a sample absorption spectrum. If absorption coefficients have not yet been determined for an entire predetermined frequency range of interest, another longitudinal mode spectral peak at the next different frequency is analyzed. In this case, the processor begins again at step 520, resulting in the determination of another sample absorption coefficient. Once absorption coefficient values spanning the frequency range of interest have been determined, the absorption coefficients are assembled into a spectrum for the frequency range of interest, as illustrated by a step 560.

## CONCLUSION

Traditional CRDS uses a high-finesse resonant optical cavity to determine an absorption spectrum of a material which interacts weakly with light. The high mirror reflectivity present in a high-finesse resonant optical cavity creates a relatively long effective interaction distance between the light and the sample. Loss at a given frequency is measured in the time domain by monitoring the decay of the intensity from the cavity output with optical detectors when the light excitation is turned off. CRDS becomes less accurate when the sample absorption is large, say  $>1000 \text{ ppm cm}^{-1}$ . In this situation, the optical cavity becomes effectively opaque and the resulting ring-down times become so short, for example  $<30 \text{ ns}$ , that the ring-down times may be difficult to measure. Under these conditions, direct absorption spectroscopy can produce more accurate results. Direct absorption spectroscopy involves directly measuring the intensity transmission through the optical cavity with a sample and comparing the results to the measured intensity transmission through an empty optical cavity. However, direct absorption spectroscopy becomes less accurate when attempting to measure small amounts of sample or samples that interact weakly with light. The exemplary systems and methods described above are particularly suitable for characterizing samples in a middle regime, between regimes better suited for CRDS and direct absorption spectroscopy.

Consider for example a resonant optical cavity constructed to have a ring-down time of  $30 \text{ ns}$ , corresponding to a baseline loss of  $1000 \text{ ppm cm}^{-1}$ . For this cavity,  $(\Delta\nu)_{FWHM}=5.3 \text{ MHz}$ , and it is possible to sweep the laser frequency at  $R \ll 88 \text{ THz s}^{-1}$  while remaining in the quasi-static regime. A spectrum may be collected by scanning the laser frequency linearly up and down over a range of  $1 \text{ cm}^{-1}$ ; a scan cycle is completed in no less than  $680 \text{ }\mu\text{s}$ . It would thus be possible to collect about 1500 scan cycles per second, from which the spectrum of the cavity may be obtained via averaging. A maximum scan rate varies as  $\tau^{-2}$ , so that a cavity constructed with a ring-down time of  $300 \text{ ns}$  could be scanned over the same frequency range at 15 scan cycles per second to remain in the quasi-static regime. The difference between the analysis of the cavity with a ring-down time of  $30 \text{ ns}$  and the cavity with a ring-down time of  $300 \text{ ns}$  illustrates the transition between the regimes in which conventional time-domain CRDS is particularly use-

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ful (large values of  $\tau$ ) and in which monitoring the transmitted intensity with direct absorption spectroscopy is particularly useful (small values of  $\tau$ ). A cavity with a ring-down time of  $30 \text{ ns}$  has an effective path length of only  $9 \text{ m}$ , so the amount of cavity enhancement is modest. Nonetheless, by taking advantage of the mode structure, it becomes possible to extract the absorption spectrum of the sample within the cavity without having to monitor the input intensity. Furthermore, the regularly-spaced cavity modes act as a built-in (relative) frequency calibration, which can remove the need for an additional precise wavelength monitor. The present invention seeks to perform self-referencing cavity enhanced spectroscopy accurately in low finesse optical cavities with high material absorption properties where CRDS is largely ineffective.

Both intensity ratio analysis and curve-fitting analysis as described above may be considered conceptually to be examples of a generalized curve-fitting approach, with intensity ratio analysis effectively fitting two intensity values of a longitudinal spectral peak (the special points of the maximum and minimum) to a model of the peak, and curve fitting analysis fitting a larger number of intensity values to the model.

It will be clear to one skilled in the art that the embodiments described herein may be altered in many ways without departing from the scope of the invention. For example, frequency scanning as described above need not be linear, but may be performed according to a sinusoidal sweep, or another sweep function that ideally is sufficiently slow. Accordingly, the scope of the invention should be determined by the following claims and their legal equivalents.

What is claimed is:

1. A spectroscopy apparatus comprising:

- a resonant optical cavity configured to hold a sample;
- an optical detector configured to detect optical signals emitted from the optical cavity and generate electrical signals from the optical signals, the optical signals defining a plurality of intensity values characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and
- a processor electrically connected to the optical detector and configured to determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak, wherein the at least two intensity values comprise a maximum intensity and a minimum intensity characterizing the longitudinal mode resonance spectral peak, and wherein the processor is configured to perform at least one of:
  - i. determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging a maximum intensity of the longitudinal mode resonance spectral peak and a maximum intensity of an immediately neighboring longitudinal mode resonance spectral peak, and
  - ii. determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by averaging a minimum intensity of the longitudinal mode resonance spectral peak and a minimum intensity of an immediately neighboring longitudinal mode resonance spectral peak.



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2. The apparatus of claim 1, wherein the processor is configured to determine the sample absorption coefficient according to a ratio of the maximum intensity to the minimum intensity.

3. The apparatus of claim 2, wherein the processor is configured to determine the sample absorption coefficient according to a logarithm of a function of the ratio.

4. The apparatus of claim 2, wherein a ring-down time of the optical cavity is less than 60 ns.

5. The apparatus of claim 1, wherein the processor is configured to determine the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging the maximum intensity of the longitudinal mode resonance spectral peak and the maximum intensity of the immediately neighboring longitudinal mode resonance spectral peak.

6. The apparatus of claim 1, wherein the processor is configured to determine the minimum intensity characterizing the longitudinal mode resonance spectral peak by averaging the minimum intensity of the longitudinal mode resonance spectral peak with the minimum intensity of the immediately neighboring longitudinal mode resonance spectral peak.

7. The apparatus of claim 1, wherein the processor is configured to perform at least one function selected from:

determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by fitting a curve over a plurality of points of the longitudinal mode resonance peak; and

determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by fitting a curve to a plurality of points of the longitudinal mode resonance peak.

8. The apparatus of claim 7, wherein the processor is configured to determine the maximum intensity characterizing the longitudinal mode resonance spectral peak by curve fitting.

9. The apparatus of claim 7, wherein the processor is configured to determine the minimum intensity characterizing the longitudinal mode resonance spectral peak by curve fitting.

10. The apparatus of claim 1, wherein the processor is configured to determine the sample absorption coefficient by fitting at least three intensity values characterizing the longitudinal mode resonance spectral peak to the model of the longitudinal mode resonance spectral peak.

11. The apparatus of claim 1, wherein the processor is configured to determine the sample absorption coefficient by fitting a curve to a shape of the longitudinal mode resonance spectral peak.

12. The apparatus of claim 11, wherein the ring-down time of the optical cavity is greater than or equal to 10 ns.

13. The apparatus of claim 11, wherein fitting the curve is performed over a frequency range encompassing two cavity free spectral ranges.

14. The apparatus of claim 11, wherein the processor is configured to generate an absorption spectrum according to successive curve fittings of longitudinal mode resonance spectral peaks.

15. The apparatus of claim 1, wherein the processor is further connected to a monochromatic light source optically coupled to the resonant optical cavity, the processor being configured to control the monochromatic light source to scan the frequency of light emitted by the light source over the range of frequencies spanning the plurality of longitudinal mode resonance spectral peaks of the resonant optical cavity.

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16. The apparatus of claim 1, wherein the processor is configured to assemble a plurality of absorption coefficients to generate an absorption spectrum for the sample.

17. The apparatus of claim 1, wherein the cavity is a confocal cavity.

18. The apparatus of claim 1, further comprising a spatial optical filter positioned in an optical path between the cavity and the optical detector, and configured to filter out higher-order transverse modes from the light incident on the optical detector.

19. The apparatus of claim 1, further comprising a second optical detector positioned outside the cavity to detect light emitted by a light source and reflected by an input mirror of the cavity, the light source being external to the cavity, wherein the processor is configured to determine the sample absorption coefficient according to an optical power indicator signal received from the second optical detector.

20. A non-transitory computer-readable medium storing instructions which, when executed by a hardware processor, cause the processor to:

receive electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and

determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak, wherein the at least two intensity values comprise a maximum intensity and a minimum intensity characterizing the longitudinal mode resonance spectral peak, and wherein the instructions further cause the processor to perform at least one of:

i. determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging a maximum intensity of the longitudinal mode resonance spectral peak and a maximum intensity of an immediately neighboring longitudinal mode resonance spectral peak, and

ii. determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by averaging a minimum intensity of the longitudinal mode resonance spectral peak and a minimum intensity of an immediately neighboring longitudinal mode resonance spectral peak.

21. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the sample absorption coefficient according to a ratio of the maximum intensity to the minimum intensity.

22. The computer-readable medium of claim 21, wherein the instructions cause the processor to determine the sample absorption coefficient according to a logarithm of a function of the ratio.

23. The computer-readable medium of claim 21, wherein a ring-down time of the optical cavity is less than 60 ns.

24. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging the maximum intensity of the longitudinal mode resonance spectral peak and the maximum intensity of the immediately neighboring longitudinal mode resonance spectral peak.

25. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the mini-



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imum intensity characterizing the longitudinal mode resonance spectral peak by averaging the minimum intensity of the longitudinal mode resonance spectral peak with the minimum intensity of the immediately neighboring longitudinal mode resonance spectral peak.

26. The computer-readable medium of claim 20, wherein the instructions cause the processor to perform at least one function selected from:

determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by fitting a curve over a plurality of points of the longitudinal mode resonance peak; and

determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by fitting a curve to a plurality of points of the longitudinal mode resonance peak.

27. The computer-readable medium of claim 26, wherein the instructions cause the processor to determine the maximum intensity characterizing the longitudinal mode resonance spectral peak by curve fitting.

28. The computer-readable medium of claim 26, wherein the instructions cause the processor to determine the minimum intensity characterizing the longitudinal mode resonance spectral peak by curve fitting.

29. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the sample absorption coefficient by fitting at least three intensity values characterizing the longitudinal mode resonance spectral peak to the model of the longitudinal mode resonance spectral peak.

30. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the sample absorption coefficient by fitting a curve to a shape of the longitudinal mode resonance spectral peak.

31. The computer-readable medium of claim 30, wherein the ring-down time of the optical cavity is greater than or equal to 10 ns.

32. The computer-readable medium of claim 30, wherein fitting the curve is performed over a frequency range encompassing two cavity free spectral ranges.

33. The computer-readable medium of claim 30, wherein the instructions cause the processor to generate an absorption spectrum according to successive curve fittings of longitudinal mode resonance spectral peaks.

34. The computer-readable medium of claim 20, wherein the instructions cause the processor to control a monochromatic light source to scan the frequency of light emitted by the light source over the range of frequencies spanning the plurality of longitudinal mode resonance spectral peaks of the resonant optical cavity, wherein the monochromatic light source is optically coupled to the resonant optical cavity.

35. The computer-readable medium of claim 20, wherein the instructions cause the processor to assemble a plurality of absorption coefficients to generate an absorption spectrum for the sample.

36. The computer-readable medium of claim 20, wherein the cavity is a confocal cavity.

37. The computer-readable medium of claim 20, wherein the instructions cause the processor to determine the sample absorption coefficient according to an optical power indicator signal received from a second optical detector positioned outside the cavity to detect light emitted by a light source and reflected by an input mirror of the cavity, the light source being external to the cavity.

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38. A computer system comprising a hardware processor and associated memory configured to:

receive electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and

determine, from the electrical signals, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak, wherein the at least two intensity values comprise a maximum intensity and a minimum intensity characterizing the longitudinal mode resonance spectral peak, and wherein the processor is configured to perform at least one of:

i. determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging a maximum intensity of the longitudinal mode resonance spectral peak and a maximum intensity of an immediately neighboring longitudinal mode resonance spectral peak, and

ii. determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by averaging a minimum intensity of the longitudinal mode resonance spectral peak and a minimum intensity of an immediately neighboring longitudinal mode resonance spectral peak.

39. A method comprising:

receiving electrical signals generated from optical signals emitted from a resonant optical cavity configured to hold a sample, the optical signals characterizing a response of the sample to light in the optical cavity as a frequency of the light is scanned over a range of frequencies spanning a plurality of longitudinal mode resonance spectral peaks; and

determining, from the electrical signals and using a hardware processor, a sample absorption coefficient by fitting at least two intensity values characterizing a longitudinal mode resonance spectral peak to a model of the longitudinal mode resonance spectral peak, wherein the at least two intensity values comprise a maximum intensity and a minimum intensity characterizing the longitudinal mode resonance spectral peak, and wherein the processor is configured to perform at least one of:

i. determining the maximum intensity characterizing the longitudinal mode resonance spectral peak by averaging a maximum intensity of the longitudinal mode resonance spectral peak and a maximum intensity of an immediately neighboring longitudinal mode resonance spectral peak, and

ii. determining the minimum intensity characterizing the longitudinal mode resonance spectral peak by averaging a minimum intensity of the longitudinal mode resonance spectral peak and a minimum intensity of an immediately neighboring longitudinal mode resonance spectral peak.